KOKAI S58-199185

SPECIFICATION

1. Title of the Invention

Water Image Sheet And Method for Its Production

2. What Is Claimed Is

1. A water image sheet comprising a transparent film substrate and, provided on its one-side surface, a liquid-absorbable lower coating layer formed of a white pigment with low refractive index, a black or dark coloring matter and a binder and a liquid-absorbable upper coating layer formed of a white pigment with low refractive index and a binder;

the pigment, the coloring matter and the binder in the lower coating layer being in a weight of 7 to 15 g/m^2 in total, and the pigment and the binder in the upper coating layer being in a weight of 8 to 25 g/m^2 in total.

2. A method for producing a water image sheet, comprising:

first coating a transparent film substrate on one-side surface thereof with an aqueous coating liquid, followed by drying to form a liquid-absorbable lower coating layer; the transparent film substrate having a surface tension of 35 dyne/cm or more or having been so surface-treated as to have a surface tension of 35 dyne/cm or more, and the aqueous coating

liquid being composed of a white pigment with low refractive index, a black or dark coloring matter and a binder, containing the pigment, the coloring matter and the binder in a mixing weight ratio of 1 : 0.4 to 1 and having a surface tension equal to or lower than that of the transparent film substrate, and being so coated that the pigment, the coloring matter and the binder are in a weight of 7 to 15 g/m^2 in total; and

then coating the lower coating layer on the surface thereof with an aqueous coating liquid, followed by drying to form a liquid-absorbable upper coating layer; the aqueous coating liquid being composed of a white pigment with low refractive index and a binder, containing the pigment and the binder in a mixing weight ratio of 1 : 0.4 to 1, and being so coated that the pigment and the binder are in a weight of 8 to 25 g/m^2 in total.

3. Detailed Description of the Invention

This invention relates to a water image sheet and a method for its production. The water image sheet termed in the present invention refers to an opaque sheet which is white or light-colored in external appearance, comprising a transparent film and, provided on one side thereof, a coating layer with specific structure, and being so made up that, when the sheet is superposed on any printed material and the side of the coating layer is soaked with a liquid

such as water, the coating layer turns transparent and a print of the printed material stands out through the film.

Conventionally, paper, what is called water image paper, which is so made up that a specific printed material is directly coated thereon with a specific aqueous coating liquid to hide the printed material so that the hidden portion can be soaked with a liquid such as water to make a visible image appear, is utilized in picture books and toys for infants and children.

In such water image paper, however, a printed material having been finished as a commercial product is coated thereon with the aqueous coating liquid. Hence, it has disadvantages that (1) where the surface of the printed material is water-repellent, it repels the aqueous coating liquid and can not be coated therewith, (2) where printing inks have weak water resistance, the print itself may be damaged, (3) since the printed material requires size corresponding to a production lot, it is too large for what is demanded in individual water image paper. These have hindered the water image paper from being popularized.

Taking note of the fact that these are due to how the coating layer, which is a medium of water images, combines with a specific printed material, an object of the present invention is to provide a water image

sheet in which the printed material is separated from the medium and the medium is combined with the transparent film so as to be utilizable in any printed materials.

Incidentally, a sort of synthetic paper is disclosed in which, for the purpose of use in printing or in drawing, a film is coated with a white pigment. In such synthetic paper, the film is merely a support and has no special function, and is also a film in which its coating layer side is made to have adaptability to uses in printing or the like. Thus, it is not the film that utilizes a high transparency inherent in the film after soaking with water as aimed in the present invention.

The present inventors have made various studies on the function and structure of such a water image sheet. As the result, as a water image sheet having structure most suited for the object of the present invention, they herein provides a water image sheet characterized in that it has a transparent film substrate and, provided on its one-side surface, a liquid-absorbable lower coating layer formed of a white pigment with low refractive index, a black or dark coloring matter and a binder and a liquid-absorbable upper coating layer formed of a white pigment with low refractive index and a binder;

the pigment, the coloring matter and the binder

in the lower coating layer being in a weight of 7 to 15 g/m^2 in total, and the pigment and the binder in the upper coating layer being in a weight of 8 to 25 g/m^2 in total.

Such a water image sheet according to the present invention is, as shown in Fig. 1, constituted of a transparent film 1, a lower coating layer 2 and an upper coating layer 3.

This water image sheet has a white or light-colored highly opaque external appearance. The coating layer is very readily water-absorbable and turns transparent upon water absorption, so that a transparent sheet united with the transparent film is formed. However, the coating layer by no means comes off even upon water absorption, and returns to its original form upon evaporation of water. That is, stated more specifically, the water image sheet has characteristic features that:

1) when dry, it is an opaque sheet in which a coating layer standing opaque and the transparent film are united;

2) after water absorption, it is a transparent sheet in which a coating layer having turned transparent and the transparent film are united; and

3) even when the water absorption and the drying are repeated, the sheet does not wrinkle, break or so, and also the coating layer by no means come off the

transparent film.

Requirements for constituting the water image sheet are also as listed below:

(1) Transparent film must be used:

Polyethylene film, polyvinyl chloride film, polypropylene film, polyester film, polyethylene terephthalate film, polyvinyl alcohol film, nylon film, acetate film, cellophane, and besides water-resistant transparent films, or transparent films endowed with water resistance, any of which can be the substrate of the water image sheet.

The higher the transparency is, the better. In regard to polypropylene film and polyester film, each of which the present inventors have selected as one of most preferred films, transparency has been measured with a photovoltaic photoelectric reflectometer Model 670 to find that the both are 5 or less in transparency and are so transparent that any value of less than that can not be found. In the present invention, however, it is enough for the film to be sensuously transparent, and its transparency is by no means limited to this value in respect of some printed materials to be seen through the film.

(2) Transparent film having surface tension of 35 dyne/cm or more must be used:

Any of the films must have a surface tension of at least 35 dyne/cm or more, and preferably 40 dyne/cm

or more. This is because, since the water image sheet is used in relation to water and also used repeatedly, the film is required to have surface strength (peel resistance) in both dry and wet states.

Table 1 shows surface tension of various high polymers (Paper Conversion Handbook, published by Shigyo Times Co., Ltd., page 37).

Table 1

High polymer	Surface tension
Polypropylene film	29
Polyethylene (linear) film	31
Polyethylene (branched) film	31
Polystyrene film	33
Polyvinyl acetate film	36
Polyvinyl alcohol film	37
Polyvinyl chloride film	39
Polymethyl methacrylate film	39
Polyvinylidene chloride film	40
Polyethylene terephthalate film	43

According to Table 1, few high polymers have the preferable surface tension, and also many of general-purpose resins have not come up with the minimum surface tension noted in the present invention.

Accordingly, in order to complete the water image sheet, it is desirable to carry out surface treatment of the transparent film. For example, it is necessary to carry out corona discharge treatment, or to coat the film thin with a solvent solution of polyvinyl alcohol, acetyl cellulose, isocyanate or the like to keep up the surface tension to the desired value.

Incidentally, needless to say, the transparent film should be colorless or light-colored and have no pattern, in view of the object of the present invention.

(3) Coating layer must have lower coating layer and upper coating layer double-layer structure:

In both the coating layers, as the white pigment, one having a refractive index of 1.7 or less is used, as exemplified by synthetic silica, talc, clay, and calcium carbonate. The use of one having a high refractive index, such as titanium oxide or the like, is not preferable for the achievement of the object of the present invention. It, however, is not restrictive to use it auxiliarily.

As the binder, casein, starch, a synthetic latex, a cellulose derivative or the like may be used, for example. In order to make the pigment combine strongly with the transparent film, a binder having a good affinity for the film and also have a transparency may be selected. In particular, an acrylic latex or an SBR

latex is preferred.

What differs in components between the lower coating layer and the upper coating layer is that a black or dark coloring matter, e.g., carbon black is contained in the lower coating layer in a small quantity. The dark (color) refers to, e.g., purple, brown, dark blue or the like. Any of these coloring matters may be used in an amount of from 1.3 to 1.7%, and preferably about 1.5%, based on other solid matter (pigment and binder). The coloring matter enriches hiding properties, but its use in a large quantity lowers the whiteness of the surface of the water image sheet and also lowers the sharpness of visible images at the time of water absorption. If on the other hand it is not added at all, the hiding properties lack. Accordingly, the coloring matter may be used in a quantity made larger or smaller or changed, in relation to the hue of the intended printed material.

(4) Mixing ratio of pigment with low refractive index to binder in each coating layer must be within specific range:

The mixing ratio of these is set to a point of proportion at which the surface strength of the water image sheet and the function to turn transparent upon water absorption can best be brought out. That is, if the binder is in a too small quantity, a weak surface strength may result, and its use in a too large

quantity may make water absorption difficult. Thus, in the present invention, the pigment and the binder are used in a mixing ratio of 1 : 0.4 to 1 in weight ratio. Although in this way the mixing ratio of the binder to the pigment is very higher than that in commonly available coated paper, e.g., coated paper and art paper, the water absorption properties are not obstructed. This is due to appropriate selection of the pigment with low refractive index and the binder.

(5) Coating must be in large coating weight:

In respect of the lower coating layer, coating is carried out in a coating weight ranging from 7 to 15 g/m^2. In respect of the upper coating layer, coating is carried out in a coating weight ranging from 8 to 25 g/m^2. If the total of coating weight in both the layers is 40 g/m^2 or more, their internal bond may lower to cause cracks in the coating layers. If on the other hand it is 15 g/m^2 or less, their hiding properties may greatly lower.

In respect of the water image sheet having satisfied the above requirements, its transparency before and after water absorption was judged. Macbeth reflection densitometer was used therefor. On its black standard density plate (density: 1.82), samples were placed to read their densities. Results obtained are shown in Table 2. Here, in each sample, the coating layer is formed under the same conditions, and

coating weight is 35 g/m^2. Also, as a comparative example, a sheet making use of paper as the substrate is shown in Table 2.

Table 2

	Transparent film (or paper)			Water image sheet	
	Thickness (μ)	Reflection density (about)	Opaqueness	Reflection density	Repeated use
Polypropylene film:					
Before WA	30	1.82	≤5	0.32	
After WA	-	-	-	0.96	possible
Polyester film:					
Before WA	53	1.82	≤5	0.25	
After WA	-	-	-	0.85	possible
Glassine paper:					
Before WA	35	-	22	0.23	
After WA	-	-	-	0.65	Impossible

WA: water absorption

As is clear from these results, the water image sheets making use of films as substrates do not so differ from the glassine paper in hiding power when

they are dry, but produce a considerable difference in transparency after water absorption.

Incidentally, the opaqueness of the water image sheet before and after water absorption is omitted, because carbon black is contained in the coating layer and hence the opaqueness can not accurately be measured. Accordingly, in respect of the water image sheet, the reflection density is used to express the hiding power or transparency. It means that, the closer to zero the reflection density is, the larger the hiding power is, i.e., the more opaque the sheet is, and also that, the closer to 1.82 it is, the more transparent the sheet is.

The water image sheet may be produced by a process comprising the steps of:

1) preparing the support film;

2) preparing an aqueous coating liquid for the lower coating layer;

3) preparing an aqueous coating liquid for the upper coating layer;

4) forming the lower coating layer by coating, followed by drying; and

5) forming the upper coating layer by coating, followed by drying;

and may be produced using a commonly available coating machine. The respective steps are described below in detail.

1) Preparation of support film:

As the support film, used is the film having a surface tension of 35 dyne/cm or more, and preferably 40 dyne/cm or more, as described previously. This is a requirement for the achievement of the stated surface strength required in the water image sheet as a product and also a requirement for the coating with the aqueous coating liquid. A film having a surface tension of less than 35 dyne/cm has a poor wettability to the coating liquid to make uniform coating difficult, and tends to be scratched also after the upper coating layer has been formed by coating. Of course, the stated surface strength is not achievable. Accordingly, any film not satisfying the requirement of surface tension must be subjected to the surface treatment by corona discharging as described previously, or to pretreatment with a suitable surface-treating agent, to keep up the surface tension to the stated level.

2) Preparation of aqueous coating liquid for lower coating layer; and

3) Preparation of aqueous coating liquid for upper coating layer:

In preparing both the aqueous coating liquids, attention is so paid that the aqueous coating liquid obtained by mixing the respective components described previously may have a surface tension smaller than, or

at most equal to, the surface tension of the transparent film. For example, where the coloring matter has a surface tension of 45 dyne/cm, the coating liquid is so prepared as to have a surface tension of 35 dyne/cm. Under such conditions, optimum conditions are prescribed also in respect of the coating weight of the lower coating layer when a stated coating apparatus is used. In the case as exemplified above, best coating operation, surface strength and so forth are achievable in a coating weight of about 10 g/m^2. Like conditions may be applied also in forming the upper coating layer by coating. In the present invention, the coating weight of the upper coating layer is usually made larger than the coating weight of the lower coating layer, and hence it is controlled by the concentration of coating liquids. Best results are obtainable when the coating weight is 15 to 20 g/m^2. Incidentally, where it is necessary to lower the surface tension of the coating liquid to keep balance with the surface tension of the transparent film, a nonionic or anionic surface-active agent, e.g., Newcol 864 (Nippon Nyukazai Co., Ltd.) or the like may be used in a small quantity.

4) Formation of lower coating layer by coating, followed by drying; and

5) Formation of upper coating layer by coating, followed by drying:

The upper coating layer is formed by coating when the lower coating layer is dried to have a water content of at most 5% or less. In this state, the structure of the lower coating layer is fixed, where micropores in the interior of the structure are formed to make easy the coating operation of the upper-layer coating liquid and also the stated surface strength is obtained after the upper coating layer has been dried.

The water image sheet thus produced may be provided with an adhesive on its back, or, as shown in Fig. 2, a pressure-sensitive adhesive 4 applied may be covered with a release paper 5 to provide a form of a tack sheet so that it can be stuck to any desired printed material, or it may be heat-sealed as it is so as to be used as the water image sheet, where not only the disadvantages the conventional products described previously have had can be eliminated, but also even the types of printed materials need not be taken into account. More specifically, the water image sheet of the present invention can widely be used without regard to materials and types of articles, on, e.g., loose materials such as napkin paper and cloth, patterns provided on wood, metal, glass, pottery and so forth, and curved-surface articles such as bottles, to which the conventional water image paper has not been applicable. A non-volatile liquid as exemplified by fluid paraffin or the like may also be used, where

visible images can be held over a long period of time. This is like the case of the conventional water image paper. Further, the coating surface of the water image sheet according to the present invention has a high surface strength as described previously, and hence is printable as usual, or freely inscribable using pencils, ball point pens or the like. Besides, so as to be used as what is called water brush paper, the water image sheet of the present invention may also be used in the state it is laminated to a sheet having any desired background color.

The present invention is specifically described below by giving Examples. In the following, "part(s)" refers to "part(s) by weight".

Example 1

A substrate formed of a 30 μ thick polypropylene film having been treated by corona discharging to have a surface tension of 45 dyne/cm was coated with a lower-layer coating liquid composed of:

water	67.65 parts
sodium hexametaphosphate	0.14 part
kaolin	7.92 parts
synthetic silica	11.10 parts
acrylate copolymer latex	12.67 parts
carbon black	0.52 part

(MIKUNI SM BLACK, registered trademark of Mikuni Color Works Ltd.)

and having a surface tension of 35 dyne/cm, by means of Mayer bar in a coating weight of 10 g/m^2, followed by drying with 100°C hot air. Subsequently, this was further coated thereon with a upper-layer coating liquid composed of:

water	65.0 parts
sodium hexametaphosphate	0.16 part
kaolin	8.7 parts
synthetic silica	13.94 parts
acrylate copolymer latex	12.20 parts

and having almost the same surface tension as the lower-layer coating liquid, by means of Mayer bar in a coating weight of 15 g/m^2, followed by drying with 100°C hot air to produce a water image sheet.

This sheet was coated on the opposite side thereof with an acrylic adhesive, and then laminated to synthetic paper (OJI YUPO, registered trademark) printed in multiple color. As the result, the printed material was completely hidden, but when soaked with water a sharp printed pattern appeared. Also, even when used repeatedly after it was dried, the coating layers did neither come off nor wrinkle at all.

Example 2

A water image sheet was produced using a hard vinyl chloride film (surface tension: 40 dyne/cm) having a thickness of 50 μ and not surface-treated and the same coating liquids as those shown in Example 1.

This sheet was coated on the opposite side thereof with a rubber type pressure-sensitive adhesive and provided thereon with release paper to prepare a tack sheet.

The release paper was peeled, and the water image sheet was stuck to a red toy automobile to hide its color. The water image sheet was easily stuck even to such curved surface. Thus, a use for a plastic model was opened which turns red when washed and returns to the original white when dried.

4. Brief Description of the Drawings

Fig. 1 is a sectional view showing an example of the water image sheet according to the present invention. Fig. 2 is a sectional view showing an example of a tack sheet making use of the water image sheet.

In the drawings, reference numeral 1 denotes a transparent film; 2, a lower coating layer; 3, an upper coating layer; 4, a pressure-sensitive adhesive; and 5, release paper.